. C. 6401

NOVEMBER, 1930

DEPARTMENT OF COMMERCE

UNITED STATES BUREAU OF MINES
SCOTT TURNER, DIRECTOR

INFORMATION CIRCULAR

GALLIUM, GERMANIUM, INDIUM, AND SCANDIUM

RECEIVED
DEC 12 1930
O. S. U. LIBRARY

BY

ALICE V. PETAR

OHIO STATE
UNIVERSITY LIBRARY

I. C. 6401
November, 1930.

INFORMATION CIRCULAR

DEPARTMENT OF COMMERCE - BUREAU OF MINES

GALLIUM, GERMANIUM, INDIUM, AND SCANDIUM[1]

By Alice V. Petar[2]

CONTENTS

	Page
Introduction	2
Description and properties	2
History	3
Occurrence	4
Uses	8
Production	10
List of dealers and importers	10
Markets and prices	10
Metallurgy	11
Bibliography	12
Gallium	12
Germanium	13
Indium	15
Scandium	16

---

[1] The Bureau of Mines will welcome reprinting of this article, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6401."

[2] Rare metals and nonmetals division, U. S. Bureau of Mines.

725537

INTRODUCTION

Among the rarest of the rare metals are four that are linked together by a common historical background as well as by chemical relationship. With the exception of indium, these metals are likewise characterized by the patriotic nature of the names given them by their discoverers. The existence of gallium, germanium, and scandium, was predicted by the Russian chemist, D. I. Mendeleeff some time prior to their discovery; and these elements might well have been overlooked, had not the search been stimulated by the urge to confirm the scientific hypothesis of their existence. Nowhere found in sufficient quantities to attract attention, these little known elements are nevertheless widely distributed in the earth's crust. So far they are found commercially mostly in the sulphide ores of zinc and must be considered as being largely curiosities of the zinc smelter. Recent progress in electrolytic zinc refining, however, now gives promise that the way may be open for the recovery of these very rare metals in larger quantities--possibly in quantities sufficient to permit of their finding commercial utilization.

DESCRIPTION AND PROPERTIES

Gallium.- Gallium is a grayish-white metal which in certain lights shows a bluish-green color. The luster is brilliant and metallic but tarnishes quickly. The metal is tough, but is soft enough to be cut by a knife. The most interesting property of gallium, however, is the wide range of temperature through which it remains liquid. The melting point is about 30° C., and its boiling point is in the neighborhood of 1700° C. When molten, gallium is not unlike mercury in appearance. The specific gravity varies from 5.9 in the solid state to 6.095 when liquid.

Germanium.- Until the last decade practically the entire knowledge of the properties of germanium was derived from the findings of C. Winkler, who discovered the element in 1886. Winkler described germanium as a grayish-white metal, crystallizing in regular octahedra and having a conchoidal fracture. He gave 5.469 for the specific gravity. Within recent years further information relative to the properties of the metal has been made available as a result of research carried on at Cornell University[3] between the years 1921 and 1927. L. M. Dennis and his associates found germanium to be too brittle to be drilled; and it was not possible to apply the Brinell hardness test, owing to the shattering of the blocks. The metal is harder than adularia (H. 6) but is not sufficiently hard to scratch epidote (H. 6.5), so that its hardness on Moh's scale is 6.25. The melting point is above 900° C. The investigations at Cornell definitely placed germanium in Group IV of the Periodic Table and demonstrated the similarity in the properties of germanium and its compounds to those of the other elements in the group. Germanium resembles silicon in its brittleness, high melting point, and resistance to acid and alkali solutions. Like tin, it is distinctly metallic and forms well-defined crystals.

---

[3] Dennis, L. M., Germanium: Ztschr. anorg. allgem. Chem., vol. 174, 1928, pp. 97-141.

Indium.- Indium is a soft, silver-white metal which is ductile and slightly heavier than zinc. Its comparatively low melting point (155° C.) and relatively high boiling point (1450° C.) are sufficiently unusual to make it of more than passing interest. It is stable in air at ordinary temperatures, but oxidizes rapidly when heated above its melting point, burning with a brilliant violet flame. Chemically, indium resembles zinc in some respects and is like aluminum and iron in others.

Scandium.- The properties of scandium are such that the question has frequently been raised as to whether this little-known element should be classed with the rare earths or elsewhere. In the solubility of its salts scandium resembles the rare earth elements, but it is in some respects analogous to the iron group. The metal has not been isolated, so that little is known concerning its properties beyond Mott's[4] calculation of 1200° C. for the melting point and 2400° C. for the boiling point.

The outstanding properties of gallium, germanium, indium, and scandium are summarized in the following table:[5]

Properties of gallium, germanium, indium, and scandium

Properties	Gallium	Germanium	Indium	Scandium
Atomic weight	69.9	72.5	114.8	44.1
Color	Gray-white	Gray-white	Silver-white	- -
Luster	Metallic	Metallic	- -	- -
Hardness	Soft	6.25	Soft	Soft
Specific gravity..	(5.94 (solid) (6.09 (liquid)	5.35	7.1 - 7.4	- -
Melting point	30° C.	958° C.	155° C.	1200° C.
Boiling point	1700° C.	- -	1450° C.	2400° C.

HISTORY

There is a striking similarity in the incidents surrounding the discovery and identification of gallium, germanium, and scandium. It is more than likely that their discovery was assured and probably hastened by the predictions of D. I. Mendeleeff concerning the existence of three elements which he described, and to which he gave the names eka-aluminum, eka-silicon, and eka-boron. His predictions stimulated research, and in 1875 Lecoq de Boisbaudran discovered an element having properties almost identical with those attributed to eka-aluminum, in a zinc blende from Pierrefitte in the Pyrenees. To this element he gave the name "Gallium" in honor of the old name for France.

---

[4] Mott, W. R., Volatilities of Refractory Materials: Am. Electrochem. Soc. Trans., vol. 34, 1918, p. 287.

[5] Data taken largely from J. W. Mellor (A comprehensive treatise on Inorganic and Theoretical Chemistry. Longmans, Green and Co.).

In 1886, C. Winkler, after making a number of analyses of a new silver mineral, argyrodite, from the Himmelsfürst mine near Freiberg, Saxony, found that each time the total constituents added to only 93 or 94 per cent. He therefore suspected the presence of a new element, which he was eventually successful in isolating. The properties of this element checked with those of Mendeleeff's eka-silicon, and Winkler patriotically called it "Germanium," from the Latin name Germania.

Scandium was discovered in 1879 by L. F. Nilson while studying the ytterbia derived from gadolinite and euxenite. He obtained 0.3 gram of a new earth, which closely resembled the eka-boron predicted by Mendeleeff in 1871. Nilson called the element "Scandium" in honor of his native land, the Scandinavian peninsula, where the minerals containing the earth were originally found. Later P. T. Cleve obtained 0.8 gram of scandia from 4 kilograms of gadolinite, and 1.2 grams from 3 kilograms of keilhauite.

Historically, indium has little or no relation to gallium, germanium, and scandium. It lacks the human interest of these elements, in that it was discovered more or less accidentally, and because its name is descriptive rather than patriotic. Indium was discovered in 1863 by F. Reich and T. Richter, who were examining zinc blendes from Freiberg with the spectroscope, in the hope of finding thallium. However, instead of the thallium lines, they obtained an indigo-blue line and a fainter blue line. They named the new element "Indium," from the indigo-blue lines of its spectrum.

OCCURRENCE

Gallium, germanium, indium, and scandium, like a number of other rare elements, are present in a wide variety of rocks and minerals in many parts of the world, but nearly always in insignificant quantities. In many instances their presence can be detected only by use of the spectroscope.

Gallium.- Various investigators have discovered gallium--usually spectroscopically--in iron minerals, particularly magnetite and pyrites, as well as metallic iron; in bauxite, china clays, and commercial aluminum; in manganese ores; in germanite; in meteoric iron; in certain French mineral waters, and in the sun. However, the only occurrence that gives promise of ever reaching commercial proportions is in zinc blendes. Gallium has been noted in very small quantities in blendes in Pierrefitte, Sweden; Schwarzenberg, Saxony; Alston Moor, Cumberland; Rio Tuerto, Spain; Sardinia; Peelwood, New South Wales; and within comparatively recent years in the zinc deposits of Oklahoma. The discovery of gallium in the Oklahoma zinc blendes was made more or less accidentally by F. G. McCutcheon, during 1915 when he was employed as chemist of the Bartlesville Zinc Co., Bartlesville, Okla. He noted some drops and beads resembling mercury on the surface of a leady residue from the redistillation of zinc, which had been stored for some time in a warm place. After a number of tests McCutcheon identified the material as an alloy of gallium and indium with small amounts of zinc. That even the Oklahoma zinc blendes do not offer a prolific source of supply of gallium is shown by the fact that the few grams of the gallium-indium alloy resulted from a residue weighing about 60 pounds which was obtained from the continued distillation of about 12,000 pounds of spelter.[6]

---

[6] Hillebrand, W. F., and Scherrer, J. A., Recovery of Gallium from Spelter in the United States: Jour. Ind. and Eng. Chem., vol. 8, 1916, p. 225.

Original from THE OHIO STATE UNIVERSITY

McCutcheon has estimated the gallium content of concentrates from the Joplin district to be from 3 to 5 ounces of gallium to the ton.

Germanium.- One of the few minerals in which germanium has been found in appreciable quantities is argyrodite, a sulpho-salt containing silver and germanium ($3Ag_2S.GeS_2$), in which the germanium content ranges from 5 to 7 per cent. The similar mineral canfieldite, has been found to contain 1.82 per cent germanium. However, the scarcity of these minerals precludes their being considered as commercial sources of supply. Argyrodite is found in a mine in Freiberg, Saxony, and in the silver mines of Ormo, Bolivia; canfieldite also occurs in Bolivia.

Like gallium, germanium has been noted in zinc blendes from a number of localities. In the course of experimental work on zinc oxides made from the spelter residues from a mixture of Joplin and Wisconsin ores, G. H. Buchanan[7] detected the presence of germanium, which was confirmed by subsequent tests at the Bureau of Standards. Buchanan estimated that the original ore carries 0.01 per cent germanium. Previously Urbain[8] examined zinc blende from different localities and found that 38 out of 64 specimens were germaniferous. Five of the ores came from Webb City, Mo.; Stolberg, near Aachen, Prussia; European Turkey (in 1909); Raible, Austria; and Mexico. From 550 kilos of the Mexican blende he obtained 5 grams of pure germanium. Hillebrand and Scherrer[9] have also reported the presence of germanium in sulphide ores from Sunset, Idaho, and Missouri, and in smithsonite from Almont, Colo., and Utah and Nevada.

Scütt[10] obtained spectrographic evidence of the presence of germanium in zinc blende from Devil's Bridge near Aberystwyth, Wales. He reported a germanium content of 2 to 4 per cent. A. del Campo[11] also examined 68 Spanish zinc blendes and found germanium to be present in 50 of the samples.

The presence of germanium in smithsonite from the Hudson mine, near Salem, Livingstone Co., Ky., has been noted by J. J. Müller[12], who found the GeO_2 content to be 0.01 per cent. He also found germanium to be present in the mine water of the same mine to an amount of 0.29 per cent of the total solids obtained by evaporation of the water.

---

[7] Buchanan, G. H., The Occurrence of Germanium in Missouri and Wisconsin Blendes: Jour. Ind. and Eng. Chem., vol. 9, 1917, p. 661.

[8] Urbain, G., Analyse spectrographique des blendes: Compt. rend., vol. 149, 1909, p. 602.

[9] Hillebrand, W. F., and Scherrer, J. A., Recovery of Gallium from Spelter in the United States: Jour. Ind. and Eng. Chem., vol. 8, 1916, p. 225.

[10] Scütt, W., Germanium in a British Mineral: Phil. Mag., vol. 1, 7th ser., 1926, pp. 1007-1009.

[11] del Campo, A., Estudio Espectrografico de las Blendas Españolas Anal. Fis. Quim., vol. 12, 1914, p. 80.

[12] Müller, J. H., Germanium in Smithsonite and Mine Waters: Jour. Ind. and Eng. Chem., vol. 16, 1924, pp. 604-5.

Papish[13] has noted the presence of minute quantities of germanium in silicate minerals from pegmatites and high-temperature vein deposits in many parts of the world. The presence of germanium, as determined spectrographically, was most strongly apparent in specimens of topaz, lepidolite, tourmaline, and spodumene. Thirty-four specimens of topaz from 27 different localities were examined, and all were found to be germaniferous. Recently Papish and Hanford[14] have noted the occurrence of germanium in meteorites. The specimens tested consisted of iron meteorites (siderite) from Toluca, Mexico, and Welland, Ontario; iron and silicate meteorites (siderolite) from Admire, Lyon Co., Kans., and Llano del Inca, Atacama, Chile; and meteorites (aerolite) from Estacado, Crosby Co., Tex., and Allagan, Allagan Co., Mich., in all of which germanite was detected spectroscopically. Germanium was extracted from the Toluca and Welland siderites.

Pufahl[15] gave the name germanite to a copper sulphide in a tetrahedrite mass at Tsumeb, Southwest Africa, which he found to contain 6.2 per cent germanium. A sample of germanite analysed by F. W. Kriesel[16] contained 8.70 per cent germanium and 0.76 per cent gallium.

Specimens of enargite, a fairly common copper-bearing mineral ($3Cu_2S.As_2S_5$) were investigated spectrographically for the presence of germanium by Papish, Brewer, and Holt,[17] with the result that in 13 out of 17 specimens examined, germanium was estimated to be present in quantities ranging from less than 0.001 per cent to more than 0.1 per cent. Taking advantage of the comparative abundance of some of the ore minerals, the investigators undertook to extract germanium from them, and determinations made on two samples of enargite gave the following results:

	Enargite from Central City, Colo.	Enargite from Butte, Mont.
Weight of enargite	50 grams	100 grams
Weight of GeO_2 extracted ..	0.0238 grams	0.0192 grams
Percentage of germanium ...	0.033	0.013

Although the germanium content of the enargite minerals was much less than that of argyrodite, canfieldite, and germanite, the authors were of the opinion that enargite, because of its greater abundance, could be used as a source of germanium.

---

[13] Papish, Jacob, New Occurrences of Germanium. II. The Occurrence of Germanium in Silicate Minerals: Econ. Geol., vol. 24, 1929, pp. 470-80.

[14] Papish, Jacob, and Hanford, Zaida M., Occurrence of Germanium and Arsenic in Meteorites: Science, vol. 71, 1930, pp. 269-70.

[15] Pufahl, O., Germanite, a Germanium Mineral and Ore from Tsumeb, Southwest Africa:. Metall. u. Erz, vol. 19, 1922, pp. 324-5.

[16] Kriesel, F. W., The Analysis of a New Germanium-Gallium Mineral Called "Germanite." Chem.-Ztg., vol. 48, 1924, pp. 961-3.

[17] Papish, Jacob, Brewer, F. M., and Holt, Donald, A., Germanium XXV. Arc Spectrographic Detection and Estimation of Germanium. Occurrence of Germanium in Certain Tin Minerals. Enargite as a Possible Source of Germanium. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 3031-2.

Papish, Brewer, and Holt[18] also subjected 12 tin minerals to spectrographic analysis and found traces of germanium in eight of them. The richest was cassiterite from the vicinity of Battle Mountain, Nev., in which more than 0.005 per cent of Ge was detected.

The presence of germanium in cassiterite from Finbo, Sweden, and Mamaku, New Zealand, has been noted by A. Hadding[19].

Forjaz[20] obtained spectrographic evidence of the presence of germanium in Portuguese mineral waters.

Insignificant quantities of germanium have also been reported in franckeite ($5PbS.Sb_2S_5.2SnS_2$), euxenite, and in tantalum and columbium minerals. The presence of germanium in samarskite has been variously reported and denied.

Papish[21], by means of a spectrographic method, detected traces of germanium in specimens of stannite from four different localities; upward of 1 per cent and "possibly as high as 3 per cent" in one of three specimens of Bolivian pyrargyrite; and traces of germanium in native copper.

Indium.- Many zinc blendes contain indium, frequently associated with gallium. Indium also occurs in tin and tungsten ores, and in some iron and manganese ores. F. Reich and T. Richter reported 0.1 per cent indium in the zinc blende from Freiberg. Other investigators reported the presence of smaller quantities of the element in blendes from various localities. Of 68 samples of zinc blende examined by A. del Campo y Cerdan, 37 were found to contain indium. Gallium, indium, and germanium were present in 29 specimens, gallium and indium in four, and indium alone in one specimen. No instances of germanium and indium without gallium were noted.

F. G. McCutcheon whose part in the discovery of gallium in domestic zinc blendes has already been referred to, estimates that the indium content of western concentrates ranges from traces to 15 ounces to the ton.

Scandium.- Scandium is a minor constituent of a wide variety of rocks and minerals. J. H. L. Vogt estimated that the 10-mile crust, the hydrosphere, and lithosphere of the earth contained 0.000000000x per cent of scandium. The estimate of F. W. Clark and H. S. Washington was 0.0000x per cent.[22] Spectroscopic observations indicate that scandium occurs in the sun and stars. G. Eberhard was of the opinion that scandium is one of the most widely distributed of the elements on the

---

[18] Papish, Jacob, Brewer, F. M., and Holt, Donald A., Pages 3029-30 of work cited.

[19] Hadding, A., Ueber das Vorkommen des Germaniums im Kassiterit Zeit. anorg. Chem., vol. 123, 1922, p. 171.

[20] Forjaz, A. Pereira, Spectrochemistry of Portuguese Mineral Waters; the Gerez Water: Compt. rend., vol. 186, 1928, pp. 1366-7.

[21] Papish, Jacob, New Occurrences of Germanium: Econ. Geol., vol. 23, 1928, pp. 660-670.

[22] Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry: Longmans, Green & Co., vol. V, 1924, pp. 480-1.

Original from THE OHIO STATE UNIVERSITY

earth's crust. It was found in zirconium minerals, in beryls, titanates, columbites, titanocolumbites of the rare earths, in micas, and in wolframite and cassiterite. R. J. Meyer and W. Crookes confirmed these conclusions and further reported that scandium could be detected in most of the rocks forming the earth's crust. However, the quantity of scandium present seldom exceeds 1 per cent. Scandium is present in most yttrium minerals and in many of the rare earth minerals.

The only mineral in which scandium occurs in appreciable quantities is thortveitite $(ScYt)_2Si_2O_7$, which contains 40 per cent Sc_2O_3 and 17 per cent of yttrium earths. The wolframites at Zinnwald and Sadisdorf are scandium-bearing, and H. S. Lukens has reported the presence of scandium in wolframite from Colorado

USES

Gallium, germanium, and indium possess certain interesting qualities that have attracted attention and given rise to the prophecy that their commercial utilization may be realized at some not distant time.

Gallium.- Experiments carried on at the Thomson Research Laboratory of the General Electric Co., West Lynn, Mass., about five years ago indicated that gallium was well adapted for use in thermometers for recording temperatures above 700° C. For this purpose a container of fused quartz capillary tubing was found to be most satisfactory. Previous experimental work had shown fused quartz to be superior to glass for high-temperature thermometry, but a suitable filling liquid for recording temperatures above the mercury limit was not available. The very high boiling point of gallium suggested that it might be adaptable for this purpose, but the tendency of liquid gallium to wet glass and quartz surfaces was a distinct disadvantage. It was found that the wetting was caused by the presence of oxide films and impurities, such as indium, zinc, lead, germanium, and arsenic. Later it was discovered that the surface oxides could be removed by treatment with warm dilute hydrochloric acid and that further oxidation could be prevented during manipulation by a surface coating of gallium chlorides and hydrochloric acid which was later volatilized under vacuum. The usual method of preventing oxidation in a atmosphere of gas was found prohibitive, because gallium absorbed or dissolved gases which were liberated when the thermometer was heated and quickly cooled.[23] Lead and indium, when added to pure gallium did not increase its tendency to wet quartz. Zinc and arsenic, on the other hand, make the wetting worse and consequen ly must be completely removed.

Other suggested uses for gallium are for the production of optical mirrors and as an alloy with aluminum to produce cathode material for metal vapor lamps.

---

[23] Boyer, Sylvester, Gallium-in-Quartz Thermometer Graduated to 1,000° C.: Ind. and Eng. Chem., vol. 17, 1925, pp. 1252-3.

Digitized by Google Original from THE OHIO STATE UNIVERSITY

Experiments conducted at the Bureau of Standards[24] indicated that a gallium-cadmium alloy containing 2 to 3 per cent gallium was a satisfactory constituent in the preparation of a monochromatic lamp, the gallium apparently serving to soften the cadmium and diminish its adhesion to the quartz, which latter failing had resulted in continued breakage of previously designed lamps. The Bureau of Standards also constructed an inclosed quartz vacuum lamp using an alloy of gallium and zinc,[25] similar in many respects to the cadmium-gallium lamp, which operated quite satisfactorily.

Germanium.- A number of uses have been suggested for germanium, but as yet no outstanding advantages have been demonstrated which would seem to render it better suited to these uses than other more abundant materials.

Germanium, in the form of its dioxide, and germanium salts have met with some success in the treatment of pernicious anemia.

Aluminum alloys containing germanium were prepared and tested by W. Kroll[26], who found that the addition of small quantities (1.2-1.6%) of germanium to duralumin, "lautal" and "aludur" alloys increased their strength by 1 kilogram per square millimeter and improved the rolling properties of duralumin. Kroll has also patented aluminum-magnesium alloys containing up to 5 per cent of germanium (German Patent 484,395, September 8, 1925).

The use of germanium in steel, including rustless steel, has been suggested.

Because of the relationship of germanium and silicon, L. M. Dennis and A. W. Laubengayer[27] were led to believe that the compounds of these elements would be analogous. Glasses similar to silicate glasses, but in which equimolecular amounts of germanium dioxide were substituted for SiO_2, were prepared. It was found that four types of glass--flint, dense flint, borate crown, and barium crown--were possible. These glasses had higher refractivity and dispersion than the silicate glasses, and greater density and expansivity. The hardness was about the same, but the germanium glasses melted at considerably lower temperatures than the silicate glasses.

Indium.- No commercial use of indium has been developed. Processes for its production at prices that would encourage its use even as a scientific medium, have been developed only recently, and it is not likely that it will become an article of commerce until such time as a use is discovered for which it is peculiarly adapted. The low melting point and high boiling point of indium suggest that it, like gallium, may be suitable for use in thermometers for recording very high temperatures. The use of indium in bearing metal alloys, in quantities ranging from 0.5 to 3.5 per cent, has been patented.[28]

---

[24] Bates, Frederick, A New Cadmium-Vapor Arc Lamp: U. S. Bureau of Standards Scientific Paper 371, 1920, pp. 45-50.

[25] United States Bureau of Standards, Tech. News Bull. 72, April 7, 1923.

[26] Kroll, W., Useful Aluminum Alloys. Replacement of Silicon by Germanium: Metall u. Erz, vol. 23, 1926, pp. 684-5.

[27] Dennis, L. M., and Laubengayer, A. W., Germanium Glasses: Jour. Am. Chem. Soc., vol. 47, 1925, pp. 1945-7.

[28] Firm of Neurath. Bearing-Metal Alloys. British Patent 283,862, January 17, 1927.

PRODUCTION

No figures are available for the production of gallium, germanium, indium, and scandium, and the small quantity produced and offered for sale is probably th result of laboratory research rather than commercial output.

LIST OF DEALERS AND IMPORTERS

The following dealers and importers have informed the Bureau of Mines tha they are interested in these elements and can furnish the metals or salts if want

A. D. Mackay, 26 Cortlandt St., New York, N. Y.
Varlacoid Chemical Co., 15 Moore St., New York, N. Y.
General Minerals Corporation, Suite 317-319 Mather Building,
Washington, D. C.
A. Daigger & Co., 159 West Kinzie St., Chicago, Ill.
Jungmann & Co., Inc., 3 Desbrosses St., New York, N. Y.
F. Rudloff, 15 William St., New York, N. Y.
Adolphe Hurst & Co., Inc., 422 Lexington Ave., New York, N. Y.
Foote Mineral Co., Inc., 1608 Summer St., Philadelphia, Pa.
Akatos, Inc., 114-118 Liberty St., New York, N. Y.
J. A. Samuel & Co., 220 Broadway, N. Y.
R. T. Vanderbilt Co., Inc., 230 Park Ave., New York, N. Y.
Charles Hardy, Inc., 122 E. 42nd St., New York, N. Y.
Phillipp Bros., Inc., Woolworth Bldg., New York, N. Y.
Grasselli Chemical Co., Guardian Bldg., Cleveland, Ohio.
Eimer & Amend, 201 E. 13th St., New York, N. Y.

MARKETS AND PRICES

The markets for these rare elements are apparently restricted to dealers and a few chemical firms that use small quantities for experimental work. The bu ers whose names have come to the attention of the Bureau of Mines are as follows:

A. Daigger & Co., 159 West Kinzie St., Chicago, Ill.
A. D. Mackay, 26 Cortlandt St., New York, N. Y.
George Uhe, Inc., 11 Cliff St., New York, N. Y.
American Neon Sign Co., 440-48 N. Oakley Blvd., Chicago, Ill.
Klein Bros. Lapidary Co., 7 West Madison St., Chicago, Ill.
Belmont Smelting & Refining Works, Inc., 316 Belmont Ave.,
Brooklyn, N. Y.
Varlacoid Chemical Co., 15 Moore St., New York, N. Y.
J. A. Samuel & Co., 220 Broadway, New York, N. Y.
R. T. Vanderbilt Co., Inc., 230 Park Ave., New York, N. Y.
Fisher Scientific Co., 709 Forbest St., Pittsburgh, Pa.
Raytheon Production Corporation, 55 Chapel St., Newton, Mass.
Phillipp Bros., Woolworth Bldg., New York, N. Y.
Abbott Laboratories, 14th St. and Sheridan Road,
North Chicago, Ill.

There are no regular quotations for gallium or for scandium compounds. Prices can be obtained upon application to dealers. Although the price of indium for experimental purposes has been reduced within the past two or three years, present quotations vary from $6 to $22 per gram, depending on the quality and quantity of material purchased. Germanium metal is quoted at from $8 to $12 per gram, and the finely powdered ore can be purchased at $20 to $30 per kilo.

METALLURGY

Recent references on the technology of these elements are abstracted below.

> In the purification of liquors obtained in the acid leaching of roasted zinc ores indium[29] is precipitated with cadmium and nobler metals by treatment with zinc dust. In working up this precipitated sponge for cadmium, indium is removed with the other impurities and can be partially separated from the latter by adding specially pure zinc shavings to their sulphate solution. The crude indium was purified by successive precipitations as hydroxide, and an oxide of 99.5 per cent purity (In_2O_3) was eventually obtained. 200 grams of this oxide were dissolved in 600 c.c. of water containing 120 c.c. of 96 per cent sulphuric acid, 250 grams of sodium citrate added, and the solution was made up to 1 litre. This solution was electrolyzed at room temperature, using a platinum anode and an indium or steel cathode at a cathodic current density of 2 amp./sq. dm. The indium deposit was compact and could be built up to 1 inch or more in thickness. Over 1 pound of the pure metal was recovered in this way.

In the course of investigations in connection with the manufacture of electrolytic zinc, U. C. Tainton and E. T. Clayton[30] found that:

> In the electrolysis of zinc sulphate solutions derived from the leaching of roasted Joplin concentrate violent fluctuations of current efficiency occurred, zinc deposits showed a great endency to redissolve, and sometimes no zinc was deposited at all. The ordinary impurities such as antimony, cobalt, nickel, and arsenic, which are known to produce such effects, had been removed, so that the influence of some other element in the solution was suspected. This proved to be germanium, which is found to cause serious loss in efficiency at concentrations as low as 1 mg./litre. Experiments showed that treatment of the solution with precipitated ferric hydroxide removed the germanium. Normally the ores contain sufficient iron to prevent this element entering the solution, but some of the Joplin ores are very low in iron and apparently high in germanium. The trouble was remedied by starting with a mixture of concentrates containing a sufficient total proportion of iron to effect complete removal of germanium.

---

[29] Westbrook, L. R., Indium: Recovery by Electrodeposition, Am. Electrochem. Soc., vol. 57, May, 1930, 7 pp.,(preprint); Brit. Chem. Abs., vol.49, 1930, p. 668.

[30] Tainton, U. C., and Clayton, E. T., Germanium in Relation to Electrolytic Zinc Production: Am. Electrochem. Soc., May, 1930. Advance copy, 8 pp.; Chem. and Ind. (London), vol. 49, 1930, p. 718.

BIBLIOGRAPHY

Gallium

Ato, Sunao. Separation and determination of gallium. I New method for the determination of gallium. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 12, 1930, pp. 225-9; Chem. Abs., vol. 24, 1930, p. 2689.

Boyer, S. Metallic gallium. U. S. Pat. 1,576,083, March 9, 1926; Chem. Abs., vol. 20, 1926, p. 1382.

_____ Refining gallium and indium. Brit. Pat. 256,950, Aug. 12, 1925; Chem. Abs., vol. 21, 1927, p. 3040.

_____ Gallium-in-quartz thermometer graduated to 1000° C. Ind. and Eng. Chem., vol. 17, 1925, pp. 1252-3.

Browning, Philip E. Indium, Gallium, Germanium. Mineral Foote-Notes, vol. 1, September 1917, p. 5.

_____ Index to the literature of gallium 1874-1903. Smithsonian Miscellaneous Collections, vol. 46, No. 1543, 1904, 12 pp.

Browning, Philip E., and Porter, L. E. On the quantitative separation and detectio of gallium. Am. Jour. Sci., vol. 44, 1917, pp. 221-5.

Brukl, Alfred. Quantitative analysis of gallium. III. Monatsh., vol. 52, 1929, pp. 253-9; Chem. Abs., vol. 23, 1929, p. 5433.

Dennis, L. M., and Bridgman, J. A. Gallium. Jour. Am. Chem. Soc., vol. 40, pp. 1531-61.

Fogg, H. C., and James C. The extraction of gallium and germanium from zinc oxide. Jour. Am. Chem. Soc., vol. 41, June 1919, p. 947.

Fricke, R., and Meyring, K. Chemistry of gallium. II. Ztschr. anorg. allgem. Chem. vol. 176, 1928, pp. 325-48; Chem. Abs., vol. 23, 1929, p. 1073.

de Haas, W. J., and Voogd, J. Superconductivity of gallium. Proc. Acad. Sci., Amsterdam, vol. 32, 1929, pp. 206-13; Chem. Abs., vol. 23, 1929, p. 2337.

_____ The superconductivity of gallium. Proc. Acad. Sci., Amsterdam, vol. 32, 1929, pp. 733-4; Chem. Abs., vol. 24, 1930, p. 8.

Hillebrand, W. F., and Scherrer, J. A. Recovery of gallium from spelter in the United States. Ind. and Eng. Chem., vol. 8, 1916, p. 225.

Hopkins, B. Smith. Chemistry of the rarer elements. 1923, pp. 114-115.

Iimori, S. The approximate content of gallium in the green kaolin from Tanokami. The existence of gallium in the solar chromosphere. Sci. Paper Inst. Phys. Chem. Research, Tokyo, Supplement 10, 1928, No. 8, pp. 1-4; Chem. Abs., vol. 23, 1929, pp. 2394-5.

James, C., and Fogg, H. C. The rapid concentration of germanium and gallium contained in the zinc oxide carrying them. Jour. Am. Chem. Soc., vol. 51, 1929, pp. 1459-60; Chem. Abs., vol. 23, 1929, p. 2896.

Johns, A. L., and Evans, E. J. The conductivities of dilute germanium, gallium, silver and copper amalgams. Phil. Mag., vol. 5, 1928, pp. 271-89; Chem. Abs., vol. 22, 1928, p. 1892.

Kirschman, H. Darwin, and Ramsey, J. B. The potentiometric determination of gallium. Jour. Am. Chem. Soc., vol. 50, 1928, pp. 1632-6.

Kriesel, F. W. Gallium in germanite from Tsumeb. Metall. u. Erz, vol. 20, 1923, pp. 257-9.

Mellor, J. W. A comprehensive treatise on inorganic and theoretical chemistry, Vol. 5, 1924, pp. 373-86.

Moser, Ludwig, and Brukl, Alfred. Determination and separation of rare metals from other metals. XI. The quantitative analysis of gallium, Part I. Monatsh., vol. 50, 1928, pp. 181-92; Chem. Abs., vol. 23, 1929, p. 577. Part II, Monatsh. vol. 51, 1929, pp. 325-33; Chem. Abs., vol. 23, 1929, p. 3185.

Papish, Jacob, and Holt, D. A. Gallium. I Arc spectrographic detection and estimation of gallium. II Extraction of gallium from lepidolite. Jour. Phys. Chem., vol. 32, 1928, pp. 142-7; Chem. Abs., vol. 22, 1928, p. 929.

Ramage, Hugh. Gallium in flue dust. Nature, vol. 119, 1927, p. 783.

Rao, K. R. The spectra of doubly ionized gallium and indium. Proc. Phys. Soc. (London), vol. 39, 1927, pp. 150-60; Chem. Abs., vol. 21, 1927, p. 1758.

Richards, T. W., and Boyce, S. The purification of gallium by electrolysis and the compressibility and density of gallium. Jour. Am. Chem. Soc., vol. 41, 1919, p. 133.

Uhler, H. S., and Browning, P. E. On the electrolysis and purification of gallium. Am. Jour. Sci., vol. 42, 1916, pp. 389-98.

Germanium

Bardet, Jacques, and Tchakirian, Arakel. Preparation and properties of some germanous salts. Compt. rend., vol. 186, 1928, pp. 637-8; Chem. Abs., vol. 22, 1928, p. 1741.

Briggs, T. R., McDuffie, R. O., and Willisford, L. H. Germanium. XXXI - Alloys of germanium: silver-germanium. Jour. Phys. Chem., vol. 33, 1929, pp. 1080-96; Chem. Abs., vol. 23, 1929, p. 3867.

Briggs, T. R. and Benedict, W. S. Germanium. XXXII - Alloys of germanium. A preliminary study of the system lead-germanium. Jour. Phys. Chem., vol. 34, 1930, pp. 173-177; Metals and Alloys, vol. 1, 1930, p. 627.

Browning, Philip E. Indium, gallium, germanium. Mineral Foote-Notes, vol. 1, September, 1917, pp. 9-10.

_____ On the separation of germanium from arsenic by the distillation of the chloride in the presence of a chromate. Am. Jour. Sci., vol. 46, 1918, pp. 663-5.

Buchanan, G. H. The occurrence of germanium in Missouri and Wisconsin blendes. Jour. Ind. and Eng. Chem., vol. 9, 1917, p. 661.

_____ The occurrence of germanium in zinc materials. Jour. Ind. and Eng. Chem., vol. 8, 1916, pp. 585-6.

Chamot, E. M., and Cole, H. I. Microchemical detection of germanium. Mikrochemie, vol. 4, 1926, pp. 97-102; Chem. Abs., vol. 21, 1927, p. 2450.

Dede, L., and Russ, W. Study of germanium. I - Treatment of germanite. Preparation of pure germanium dioxide and the purest germanium tetrachloride. Ber. 61B, 1928, pp. 2451-9.

Dennis, L. M. Glass containing germanium. U. S. Pat. 1,607,817, November 23, 192

______ Germanium. Z. anorg. allgem. Chem., vol. 174, 1928, pp. 97-141; Chem. Abs., vol. 22, 1928, p. 4286.

Dennis, L. M., and Papish, Jacob. Germanium. I - Extraction from germanium-bearing zinc oxide. Nonoccurrence in samarskite. Jour. Am. Chem. Soc., vol. 43, 1921, pp. 2131-43.

Dennis, L. M., and Johnson, E. B. Germanium. V - Extraction from germanium-bearing zinc oxide, etc. Jour. Am. Chem. Soc., vol. 45, 1923, p. 1380.

Dennis, L. M., Tressler, K. M., and Hance, F. E. Germanium. VI - Metallic germanium. Reduction of germanium dioxide, etc. Jour. Am. Chem. Soc., vol. 45, 1923, pp. 2033-47.

Dennis, L. M., and Laubengayer, A. W. Germanium glasses. Jour. Am. Chem. Soc., vol. 47, 1925, pp. 1945-7.

______ Germanium. XVII - Fused germanium dioxide and some germanium glasses. Jou Phys. Chem., vol. 30, 1926, pp. 1510-26.

Fogg, H. C. Germanium. Foote-Prints, vol. 3, No. 1, 1930, pp. 19-32.

Fogg, H. C., and James, C. The extraction of gallium and germanium from zinc oxid Jour. Am. Chem. Soc., vol. 41, 1919, p. 947.

Goldschmidt, V. M. The crystal and geochemical properties of germanium. Naturwissenschaften, vol. 14, 1926, pp. 295-7. Chem. Abs., vol. 20, 1926, p. 2102.

Hopkins, B. Smith. Chemistry of the rarer elements. 1923, pp. 196-7.

James, C., and Fogg, H. C. The rapid concentration of germanium and gallium contained in the zinc oxide carrying them. Jour. Am. Chem. Soc., vol. 51, 1921, pp. 1459-60.

Johns, A. L., and Evans, E. J. The conductivities of dilute germanium, gallium, silver, and copper amalgams. Phil. Mag., vol. 5, 1928, pp. 271-89.

Keil, Werner. Germanium and gallium from germanite. Z. anorg. allgem. Chem., vol. 152, 1926, pp. 101-4; Chem. Abs., vol. 20, 1926, p. 2294.

Kroll, W. Useful aluminum alloys. Replacement of silicon by germanium. Metall u Erz, vol. 23, 1926, pp. 684-5; Chem. Abs., vol. 21, 1927, p. 3879.

______ The diagram germanium-aluminum. Metall u. Erz, vol. 23, 1926, pp. 682-4; Chem. Abs., vol. 21, 1927, p. 3880.

______ Alloys of aluminum with germanium. Metallurgist, vol. 3, 1927, pp. 6-7.

Mellor, J. W. A comprehensive treatise on inorganic and theoretical chemistry. Vol. VII, 1927, p. 255.

Müller, John H. Atomic weight of germanium. Jour. Am. Chem. Soc., vol. 43, 1921, pp. 1085-95.

_____ A separation of germanium and arsenic. Jour. Am. Chem. Soc., vol. 43, 1921, pp. 2549-52.

_____ A new method for the gravimetric determination of germanium. Jour. Am. Chem. Soc., vol. 44, 1922, pp. 2493-98.

_____ Germanium in smithsonite and mine waters. Ind. Eng. Chem., vol. 16, 1924, pp. 604-5.

Papish, Jacob, Brewer, F. M., and Holt, Donalt A. Germanium. XXV - Arc spectrographic detection and estimation of germanium. Occurrence of germanium in certain tin minerals. Enargite as a possible source of germanium. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 3028-33.

Papish, Jacob. Occurrence of germanium in topaz. Science, vol. 68, 1928, pp. 350-1.

_____ New occurrences of germanium. Econ. Geol., vol. 23, September, 1928, pp. 660-70.

_____ New occurrences of germanium. II - The occurrence of germanium in silicate minerals. Econ. Geol., vol. 24, 1929, pp. 470-80.

Papish, Jacob, and Hanford, Zaida M. Occurrence of germanium and arsenic in meteorites. Science, vol. 71, 1930, pp. 269-70.

Pufahl, O. Germanite, a germanium mineral and ore from Tsumeb, Southwest Africa. Metall u. Erz, vol. 19, 1922, pp. 324-5.

Scütt, W. Germanium in a British mineral. Phil. Mag., vol. 1, 7th ser., 1926, pp. 1007-9.

Silberstein, James. Germanium, a useful metal in the future. Metal Ind. (N. Y.), vol. 25, 1927, p. 250.

Tressler, Katharina M., and Dennis, L. M. Germanium. XX - Preparation of fused germanium directly from germanium dioxide. Jour. Phys. Chem., vol. 31, 1927, pp. 1429-32.

Indium

Boyer, S. Refining gallium and indium. British Patent 256,950, August 12, 1925; Chem. Abs., vol. 21, 1927, p. 3040.

Browning, Philip E. Index to the literature of indium, 1863-1903. Smithsonian Misc. Collections, No. 1571, 1905, 15 pp.

_____ Indium, gallium, germanium. Mineral Foote-Notes, vol. 1, 1917, September, p. 3.

Browning, Philip E., and Porter, L. E. Separation of gallium from indium and zinc by fractional crystallization of the cesium-gallium alum. Jour. Am. Chem. Soc., vol. 43, 1921, p. 126.

Dennis, L. M., and Bridgman, J. A. Analysis of mixtures containing gallium, indium, zinc, and aluminum. Jour. Am. Chem. Soc., vol. 40, 1918, pp. 1549-57.

Original from THE OHIO STATE UNIVERSITY

Druce, J. G. F. Occurrence of indium in commercial iron sulphide and its extraction. Ztschr. angew. Chem., vol. 41, 1928, p. 79; Chem. Abs., vol. 22, 1928, p. 3022.

Henrich, F., Laubmann, H., and Prell. An indium-bearing sphalerite from the Oberpfälzer Wald, Bavaria. Ztschr. angew. Chem., vol. 37, 1924, pp. 877-8; Chem. Abs., vol. 19, 1925, p. 624.

Heyrovsky, J. The analytical chemistry of indium. Chem. Listy, vol. 19, 1925, pp. 168-72; Chem. Abs., vol. 20, 1926, p. 722.

Mellor, J. W. A comprehensive treatise on inorganic and theoretical chemistry. Vol. 5, 1924, pp. 387-405.

Moser, Ludwig. Chemistry and chemical technology of the rare elements. Oesterr. Chem. Ztg., vol. 26, 1923, pp. 67-70; Chem. Abs., vol. 17, 1923, p. 2843.

Thiel, A., and Luckmann, H. Indium; separation from certain associates. Ztschr. anorg. allgem. Chem., vol. 172, pp. 353-71, 1928; Chem. Abs., vol. 22, 1928, p. 4396.

Westbrook, L. R. Indium: Recovery by electrodeposition. Trans. Am. Electrochem. Soc., vol. 57 (preprint), 1930, 7 pp.

Williams, E. J. The electrical conductivity of some dilute liquid amalgams. Phil. Mag., vol. 50, 1925, pp. 589-99.

Scandium

Brogger, W. C., Vogt, Th., and Schetelig, J. The minerals of the southern Norwegian granite pegmatites. II - Silicates of the rare earths. Vid. Selsk. Skrifter, Kristiana, I Mat.-Nat. K_1. No. 1, 151 pp., 1922; Chem. Abs., vol. 17, 1923, p. 2254.

Eberhard, G. Ueber die weite Verbreitung des Scandium auf der Erde. Sitzungber. Königlich Preussischen Akad. Wissenschaften, vol. 33, 1908, Berlin, pp. 851-868.

James, C. Scandium from a Brazilian source. Jour. Am. Chem. Soc., vol. 40, 1918, p. 1674.

Lukens, Hiram Stanhope. Scandium in American wolframite. Jour. Am. Chem. Soc., vol. 35, 1913, pp. 1470-1472.

Mellor, J. W. A comprehensive treatise on inorganic and theoretical chemistry. Vol. V, 1924, pp. 480-493.

Sarkar, P. B. Scandium and rare earths. Ann. Chim., vol. 8, 1927, pp. 207-62; Chem. Abs., vol. 22, 1928, p. 4074.

Smith, N. H. The atomic weight of scandium. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 1642-50.

Spencer, J. F. The metals of the rare earths. New York, 1919, pp. 128-133.

Urbain, G., and Sarkar, P. B. The analogies of scandium with the rare earth elements and with the tervalent elements of the iron family. Compt. rend., vol. 185, 1927, pp. 593-6; Chem. Abs., vol. 22, 1928, p. 200.

Urbain, P., and Urbain, G. Extraction and purification of scandium from the thortveitite of Madagascar. Compt. rend., vol. 174, 1922, pp. 1310-3; Chem. Abs., vol. 16, 1922, p. 2647.

Winter, Herbert. Ueber Vorkommen und Reindarstellung des Scandiums. Inaugural dissertation. Friedrich-Wilhelm Universitat, Berlin, June 14, 1911, pp. 14-28.